

# Synthesis and Hydrogen Uptake Property of Rare-Earth/Transition-Metal Hydride Clusters

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Hydrogen is thought to be an ideal fuel for vehicles and portable electronics because it is non-polluting, and forms an environmentally benign by-product—water—on combustion. The recent increasing interest in hydrogen as a fuel warrants careful studies into structural chemistry of this element. Thus, the structure of soluble molecular multinuclear hydride clusters, whose cores resemble little fragments of metals with hydrogen atoms attached, have been actively investigated to understand the interactions of hydrogen with metal-containing materials for hydrogen storage and also for the development of new catalysts for hydrogen transformations.

We recently found that rare earth metal polyhydride cluster **1** can show unique structure, which possesses 4-coordinate tetrahedral hydrogen in the center of the metal core, and its unique reactivities toward a variety of unsaturated substrates.<sup>1-7</sup> During these studies, we became interested in the use of the rare earth metal polyhydride clusters as building blocks for the synthesis of rare-earth and d-block heteronuclear polyhydride clusters, which are expected to have more unique structures and properties of their own. Here we show the rare-earth and d-block heteronuclear clusters, **2a** and **2b**, which can be formed by the reaction of **1** with  $\text{Cp}^*\text{M}(\text{PMe}_3)\text{H}_5$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ). The UV irradiation of **2a** and **2b** yielded “phosphine free” clusters, **3a** and **3b**. (Fig.1). While cluster **3b** can oxidatively add one molecule of hydrogen in a process that can be reversed by UV irradiation, cluster **3a** can release one molecule of hydrogen to afford more electronically unsaturated cluster **5**, which can be reversed by the addition of hydrogen (Fig.1).

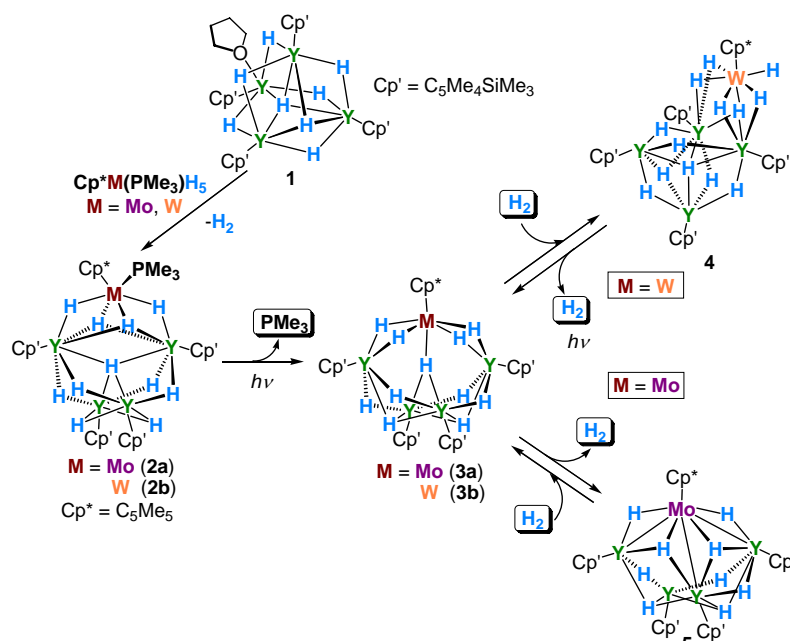
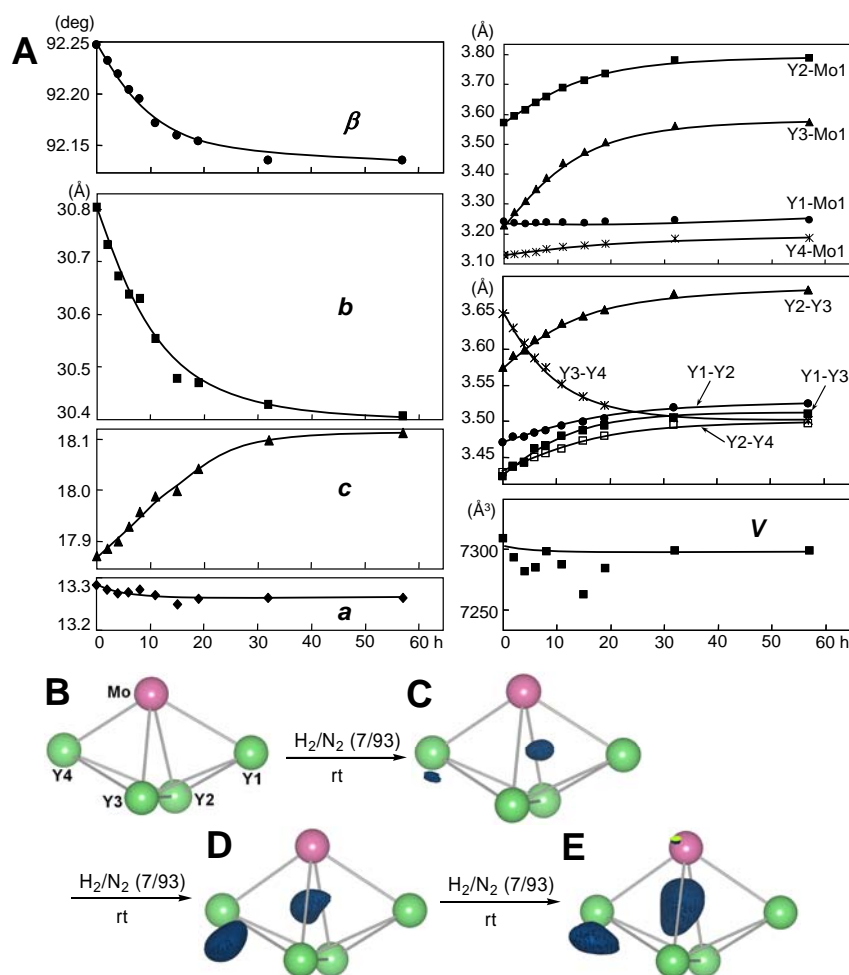


Fig.1. Synthesis of Y<sub>4</sub>-M heteropentametallc polyhydrides **2** to **5**.

Compound **5** reacts with hydrogen in the solid state. Of particular note is that in the crystalline state **5** reacts with hydrogen while retaining its crystallinity. The crystal of **5** underwent a change in unit cell dimensions without degradation of crystallinity when it was exposed to N<sub>2</sub>/H<sub>2</sub> mixed gas. Fig. 2A shows the changes in the unit cell parameters,  $a$ ,  $b$ ,  $c$ ,  $\beta$ , and  $V$ , and the average of metal–metal distances with reaction time. The  $a$ ,  $V$  values and

Y1–Mo1 distance are almost constant, while  $b$ ,  $\beta$  values and Y3–Y4 distance decrease whereas the other parameters ( $c$  axis, Y2–Mo1, Y3–Mo1, Y4–Mo1, Y1–Y2, Y1–Y3, Y2–Y3, Y2–Y4) increase. The elongation of metal–metal distances may provide the space for hydrogen atom, which is formed at the center of the metal framework cavity, while the shortening of the Y3–Y4 distance may indicate that the hydrogen atom is newly formed and bridging between Y3 and Y4. Fig. 2B–E shows the real time in situ observation of hydrogen addition reaction followed by use of composite difference electron density maps at each reaction step. A gradual increase of the



**Fig. 2.** Real time in situ observation of the hydrogen uptake process by a single crystal of **5**: (A) The change of the unit cell parameters and the average of metal–metal distances with reaction time. (B) Composite difference electron density maps created with the Visualization for Electronic and Structural Analysis (VESTA). Cp', Cp\* and hydride ligands are omitted for clarity. A crystal of **5** reacted with H<sub>2</sub>/N<sub>2</sub> mixed gas (7/93) at room temperature for 11 h (C), 19 h (D), and 57 h (E), respectively, using inner one-third data (sin $\theta$ / $\lambda$  cutoff = 0.33 Å<sup>-1</sup>). The contour surface (blue) corresponds to the value of 0.3 eÅ<sup>-3</sup>.

## References

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electron density of the hydrogens (blue color), which are in interstitial position and bridging position between Y3 and Y4, is observed as the reaction proceeds. This observation indicates that the crystal of **5** is gradually becoming the crystal of **3a**. Although there are some examples of the intra- and inter-molecular reaction retaining their crystallinity, to our best knowledge, this is the first example of an intermolecular hydrogen uptake reaction in which the single crystal integrity is fully preserved.